Bioresource Technology 111 (2012) 439–446

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

The effect of torrefaction on the chemistry of fast-pyrolysis bio-oil

Jiajia Meng, Junyeong Park, David Tilotta, Sunkyu Park *

Department of Forest Biomaterials, North Carolina State University, Raleigh, NC 27695, USA

ARTICLE INFO

Article history:
Received 5 December 2011
Received in revised form 25 January 2012
Accepted 27 January 2012
Available online 8 February 2012

Keywords:
Wood
Bio-oil
Fast pyrolysis
Torrefaction
GC/MS

ABSTRACT

Fast pyrolysis was performed on torrefied loblolly pine and the collected bio-oils were analyzed to compare the effect of the torrefaction treatment on their quality. The results of the analyses show that bio-oils produced from torrefied wood have improved oxygen-to-carbon ratios compared to those from the original wood with the penalty of a decrease in bio-oil yield. The extent of this improvement depends on the torrefaction severity. Based on the GC/MS analysis of the pyrolysis bio-oils, bio-oils produced from torrefied biomass show different compositions compared to that from the original wood. Specifically, the former becomes more concentrated in pyrolytic lignin with less water content than the latter. It was considered that torrefaction could be a potential upgrading method to improve the quality of bio-oil, which might be a useful feedstock for phenolic-based chemicals.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Thermochemical conversion of lignocellulosic biomass has received increasing attention as a strategy to produce biofuels from renewable resources. Fast pyrolysis, one of the promising thermochemical approaches, rapidly converts organic biomass into bio-oil, bio-char, and syngas in the absence of oxygen. With a residence time of less than two seconds, this simple and low-cost technology can transform various feedstocks such as agricultural and forest residues into value-added biofuels and chemicals. In addition, biofuels derived from renewable biomass contributes a positive effect on greenhouse gas emission as compared with petroleum-based transportation fuels (Reijnders, 2006). Because of these advantages, fast pyrolysis is thought to have great potential as an avenue for replacing petroleum-based fuels and chemicals.

Although fast pyrolysis has been studied over the last few decades, several unfavorable properties of its liquid product hinder its application to the production of value-added fuels and chemicals (Czernik and Bridgwater, 2004). First, owing to its high oxygen content (~40%) (Mohan et al., 2006), pyrolysis bio-oil has a relatively high chemical reactivity. For example, bio-oil components such as acids and aldehydes can engage in several types of reactions to form esters and other oligomers, resulting in higher molecular weights (Diebold, 2002). Therefore, increased viscosity and phase separation often occur to the bio-oil during storage. Second, the bio-oil is also plagued by high acidity (pH ~2) and volatility, which also lead to numerous application challenges. In short, fresh bio-oil is not suitable for direct application without stabilization and reduction of oxygen concentration in it.

Several upgrading technologies have been proposed to reduce the oxygen content of bio-oil, usually involving catalytic hydrotreating and hydrocracking (Elliott and Hart, 2009; Sharma and Bakhshi, 1993). Unfortunately, these approaches require high hydrogen consumption and their overall yield of high quality bio-oil is low (Elliott, 2007). To reduce high hydrogen demand during catalytic upgrading, fast pyrolysis on biomass having low oxygen content is a promising alternative as it should produce bio-oil with low oxygen content.

A potential method of reducing the oxygen content of biomass feedstock is through torrefaction. A mild pyrolysis process, torrefaction, occurs at 200–350 °C and is valued as an effective way to improve the thermochemical quality of biomass in its application with coal co-combustion (Prins et al., 2006a; Zwart et al., 2006; Couhert et al., 2009). Most importantly, this mild thermal pretreatment reduces the oxygen content significantly by losing water, carbon dioxide, and carbon monoxide (Yan et al., 2009). In addition, the removal of acidic components like acetic acid originating from acetoxy groups in the xylan side chain has been reported (Yan et al., 2010; Prins et al., 2006b; Bourgois and Guyonnet, 1988). As another advantage, the specific grinding energy of torrefied pine chips can be reduced to 30 kW h/t compared to 260 kW h/t of untreated pine chips (Phanphanich and Mani, 2011). It is also reported that torrefaction can reduce the size distribution of particles, where evenly sized wood particles can be utilized for the process (Repellin et al., 2010). All these advantages are potentially beneficial to the production and quality of pyrolysis bio-oil.

To the best of our knowledge, torrefaction as a pretreatment technology for fast pyrolysis to enhance bio-oil properties has not yet been reported. The work presented here puts forward an

---

* Corresponding author. Tel.: +1 919 515 0473; fax: +1 919 515 6302.
E-mail address: sunkyu_park@ncsu.edu (S. Park).

0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2012.01.159

idea of integrated torrefaction and fast pyrolysis processes. It is expected that under suitable combinations of torrefaction and pyrolysis conditions, pyrolysis bio-oil with enhanced physical and chemical properties can be produced from thermally treated biomass. The objective of this study, therefore, was focused on comparing fast pyrolysis of torrefied wood with that of non-treated wood by examining the change of the bio-oil chemistry.

2. Methods

2.1. Torrefied biomass production

Loblolly pine chips (15 by 6 mm) containing bark were used as the raw material for torrefaction. A pilot-scale torrefaction system at North Carolina State University was operated to produce torrefied wood at three different severities, which were produced at 270, 300, and 330 °C for 2.5 min respectively and referred as LP-TA, LP-TB and LP-TC in this study. The raw wood without torrefaction was named LP-Raw and the torrefaction severity increases in the series from LP-TA to LP-TC. The severity of torrefaction is often indicated by the weight loss during the torrefaction process [Almeida et al., 2010] and the products used in this study have the weight loss of 16.5%, 24.1%, and 46.5% for LP-TA, LP-TB and LP-TC respectively, based on the original weight of non-torrefied dry wood.

2.2. Pyrolysis bio-oil production

A lab-scale reactor, presented in Fig. 1, was used for the fast pyrolysis operation. The reactor consists of a screw feeder, a fluidized-bed with a diameter of 43 mm, and a liquid collection system with two water-cooling condensers and one electrostatic precipitator. Two round electric muffle furnaces were placed outside of the reactor to provide the heat source. Approximately 200 g of sand was deposited into the bottom of the pyrolysis reactor as the fluidizing and heat transfer medium. Two streams of nitrogen gas, one introduced from the bottom of the reactor and the other from the end of the feeding tube, were used as fluidizing gas. The nitrogen flow at the feeder facilitates the feeding procedure and prevents the blockage of biomass in the feeding channel. In addition, the reactor maintains an oxygen-free environment during the biomass pyrolysis.

Fast pyrolysis was performed at 500 °C with a nitrogen flow rate of 12 L/min and a biomass feeding rate of 150 g/h. The residence time was calculated to be 1.5 s. The produced pyrolysis aerosols were collected in the two condensers cooled with water at 5 °C, and the electrostatic precipitator (ESP) maintained at 12 kV. The pyrolysis bio-oils were collected at two locations, after the first condenser and after the electrostatic precipitator as shown in Fig. 1. These oils were named BOC (bio-oil after condenser) and BOP (bio-oil after precipitator), respectively.

2.3. Characterization of torrefied wood and pyrolysis bio-oil

2.3.1. Compositional analysis

An air dried woody sample (40–60 mesh) was extracted with benzene-ethanol mixture (v/v = 2:1) according to Tappi Standard T204 cm-07 for 24 h. The extraction amount was calculated by the gravimetric method of the extraction liquid after vacuum drying. The amounts of structural carbohydrates and lignin of both torrefied wood and non-torrefied wood were measured by Klason lignin analysis (Dence, 1992) followed by HPLC sugar analysis (Sluiter et al., 2008).

2.3.2. Elemental and proximate analysis

Carbon, hydrogen, and nitrogen analyses of both the biomass and bio-oil were performed according to ASTM-D5291 using a Perkin Elmer CHN Elemental Analyzer (2400 Series II). A sample size of 7 mg was used for each test, and the analyses were performed

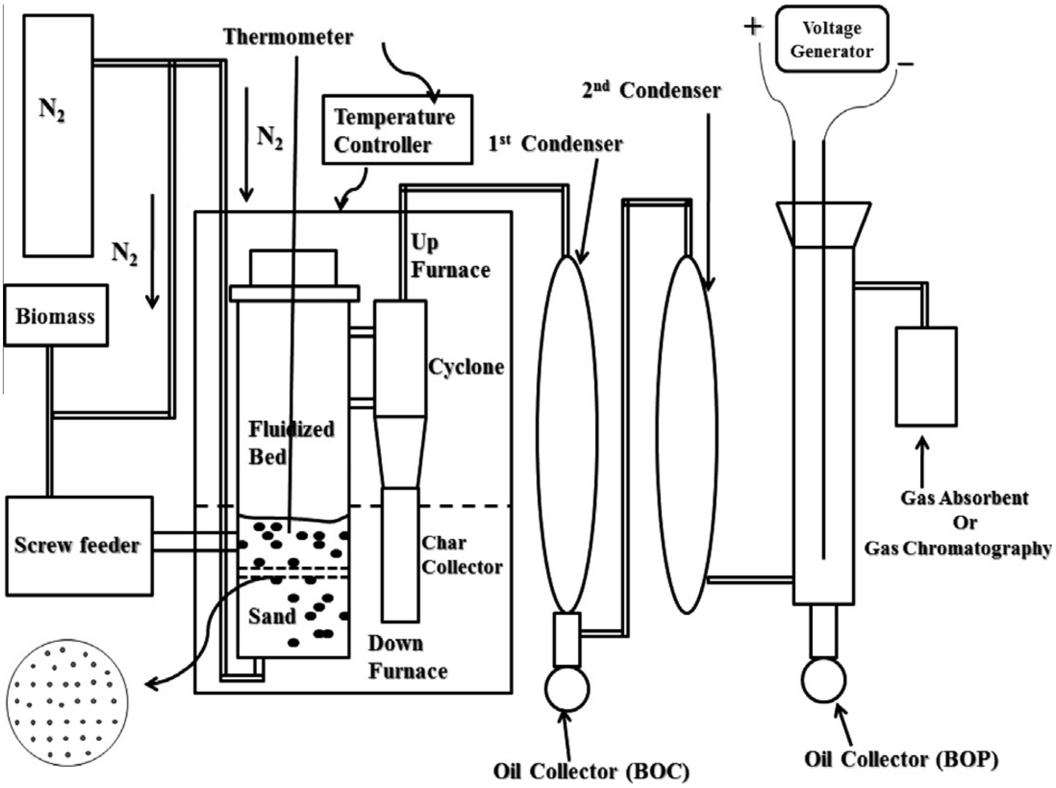

Fig. 1. Schematic diagram of lab-scale fast pyrolysis reactor.

in triplicate. The carbon, nitrogen, and hydrogen amounts were determined by this method and the oxygen contents were calculated by difference. The proximate analyses were performed with a muffle furnace according to ASTM-D1762-84.

2.3.3. Water content

The water content of the bio-oils was determined by Karl-Fischer titration according to ASTM E 203-08 using HYDRANAL Titrant 5E, HYDRANAL Solvent E and HYDRANAL Water Standard 10.0. The apparatus used was a Schott Automatic Volumetric Karl Fischer Titrator (WU-24907-00).

2.3.4. High heating value

The high heating value of both wood and bio-oil was measured according to DIN 51900 with 1108 oxygen combustion bomb (Parr Instrument Company). Prior to the analysis, the wood powder was pressed to make a tablet and 0.5 g of sample loading for both wood and bio-oil was applied for each analysis.

2.3.5. GC/MS analysis

Gas chromatographic/mass spectrometric (GC/MS) analyses of bio-oils were performed on a Finnigan Polaris Q Plus system. The MS detector was set at a full scan mode with a mass to charge range from 10 to 550 amu. Standard electron impact (EI) ionization at 70 eV was employed and the ion source temperature was 200 °C. The GC column used for separation was a DB-1701 column 60 m × 0.25 mm with 0.25 μm film thickness. The GC oven temperature was initially held at 45 °C for 4 min, then ramped at 3 °C/min to 280 °C, and held at 280 °C for 15 min. The injector and detector temperatures were set at 250 and 280 °C, respectively. The injector split ratio was fixed at 30:1. High purity helium was employed as the GC carrier gas at a flow rate of 38 cm/min, and the bio-oil sample was prepared as 6 wt.% solutions dissolved in acetone filtered through a 0.25 μm PTFE filter. 1 μL of bio-oil solutions were injected for each analysis and duplicate tests were performed for each analysis.

3. Results and discussion

3.1. Torrefied wood characterization: compositional, proximate, and ultimate analyses

Loblolly pine derived torrefied wood is considered to have a similar composition as its original wood with respect to cellulose, hemicellulose, and lignin, but the amount of each component is expected to be different depending on the torrefaction conditions. To investigate the effect of torrefaction on the composition of loblolly pine, klason lignin and sugar analysis were performed on the torrefied wood. However, klason lignin and acid soluble lignin are named in Table 1 as acid insoluble residue and acid soluble residue, respectively; because the acid hydrolysis residues of torrefied wood may be chemically and structurally different to conventional klason lignin and it may also contain thermal degradation residues from carbohydrates. As shown in Table 1, a reduction of cellulose (represented by glucan) and hemicellulose (represented by xylan, galactan, arabinan and mannan) was noticed as the torrefaction intensity increased. The reduction rate of hemicelluloses is higher than that of cellulose. For the LP-TB sample, 51.3% of the hemicellulose loss (18.7–9.1%) is realized and the cellulose loss is identified as 11.4% (36.1–32.0%). While both the hemicelluloses and cellulose had an intense thermal degradation, it should be noted that lignin was relatively preserved. This result can be explained by the different thermal reactivity of the three major wood components. According to thermogravimetric analysis of the isolated biomass components (data not shown here), hemicellulose (beech wood xylan from Sigma–Aldrich) is the most reactive compound and its major decomposition temperature resides around 275 °C. Followed by hemicellulose, cellulose (Avicel PH-101 from Sigma–Aldrich) mainly decomposes at 325 °C and lignin (alkali lignin from Sigma–Aldrich) has a very slow decomposition profile which peaks at 375 °C. The torrefaction temperature used in this study is in the range of 280–350 °C which exceeds the temperature where maximum hemicellulose decomposition occurs but also resides in the early decomposition range of cellulose.

The original extractives in the raw biomass are expected to be extensively removed during the torrefaction because of the intense thermal pretreatment. However, Table 1 shows an increasing amount of the extractable compounds for the torrefied wood. GC/MS data of these extractives for torrefied wood (data not shown) indicates that they are different from the original extractives in LP-Raw but similar to the composition of bio-oils, i.e., their major compositions are levoglucosan and lignin fragments. The generation of these distinct extractives originates from the torrefaction. Thermal decomposition of wood components destroys its matrix and increases the extractable fractions in the wood. Some of these heavy fractions (moderate molecular weights) with high boiling points resided in the wood and became extractable while others (compounds with lower boiling points) went to the vapor phase during torrefaction.

Table 2 shows the results of the proximate and ultimate analyses of the wood samples. These analyses are useful in gaining a better comprehension of how these feedstocks differ in terms of their fuel properties. It is worthwhile to state that, other than the conventional ‘moisture content’ expression in Table 2, the term ‘highly volatile’ content is applied because measuring the moisture content at 105 °C by using an oven drying method is not appropriate for torrefied wood. Simply, some of the extractives, as discussed above, will be released during the drying process. The weight loss of these condensates should not be significant; therefore the change of highly volatile content within the four samples can still be representable for the variance of moisture content among them. Fast pyrolysis usually requires the water content of the feedstock be typically less than 10% (Mohan et al., 2006). As received however, biomass, being hydrophilic in nature, has a moisture content in the range of 50–60% (wet basis) (Demirbas, 2004) and requires

Table 1
Total carbohydrate analyses of torrefied wood.

Sample ID	Carbohydrate (%)					Lignin (%)			Extractives (%)
	Glucan	Xylan	Galactan	A&M[a]	Total	AIR[b]	ASR[c]	Total	
LP-Raw	36.1	6.4	2.3	10.0	54.8	30.1	1.6	31.7	2.1
LP-TA	34.4	4.2	1.0	7.0	46.6	41.0	1.8	42.8	5.8
LP-TB	32.0	3.0	0.7	5.4	41.1	48.1	1.8	49.9	6.0
LP-TC	18.0	0.4	0.0	0.6	19.0	74.2	2.6	76.8	10.4

[a] A&M: arabinan and mannan.
[b] AIR: acid insoluble residue, usually termed as klason lignin.
[c] ASR: acid soluble residue, usually termed as acid soluble lignin.

Table 2
Proximate and ultimateanalyses of torrefied wood.

Sample ID	HHV[a] (MJ/kg)	HVC[b] (%)	VM[c] (%)	FC[d] (%)	Ash (%)	C (%)	H (%)	O (%)	N (%)	O/C[e]
LP-Raw	20.0 (18.2)	9.3	84.6	14.8	0.56	50.5	6.26	42.6	0.09	0.63
LP-TA	22.7 (20.8)	8.1	78.6	20.8	0.62	55.0	5.94	38.3	0.11	0.52
LP-TB	24.0 (22.1)	8.0	76.4	22.8	0.78	57.3	5.79	36.0	0.14	0.47
LP-TC	26.3 (25.2)	4.2	59.9	38.6	1.45	65.8	4.87	27.6	0.28	0.31

[a] HVV: high heating value based on dry wood (wet-based HHV in parentheses).
[b] HVC: highly volatile compounds, which include moisture and light extractives generated by torrefaction.
[c] VM: volatile matter.
[d] FC: fixed carbon.
[e] O/C: oxygen to carbon atomic ratio.

extra energy and/or time to dry it prior to being fed into a pyrolysis reactor. Other than removing water from the biomass, it does not produce any valuable products and this amount of energy and time consumption could be costly in the industry production. Table 2 shows that the water content of the torrefied wood is under 10%, and this low moisture content can be maintained during storage due to the change in hydrophobicity after the thermal pretreatment (Acharjee et al., 2011). Therefore, the additional drying step for fast pyrolysis is not necessary when torrefaction is performed as a pretreatment. Indeed, torrefaction also consumes energy, however, it can result in high quality bio-oil and reduce the energy consumption in grinding process for fast pyrolysis; on the other hand, different from the simple drying process, torrefaction produces volatiles that can be collected as byproducts and the major composition of this condensates mainly contains acetic acid and small quantities of methanol, formic acid, lactic acid, furfural and hydroxyl acetone (Prins et al., 2006a,b). Carbon dioxide and carbon monoxide with trance amount of hydrogen and methane was also detected from torrefaction gas products (Prins et al., 2006a,b). The improved bio-oil quality, reduced energy consumption in the grinding process together with the potential value of collected torrefaction volatiles may compensate the energy consumption of torrefaction to some extent. In Table 2, the volatile matter content decreases from LP-Raw to LP-TC along with the increased fixed carbon content. This can be explained by the loss of volatiles during torrefaction treatment which make the torrefied wood more concentrated in thermally non-reactive carbon. These two indices show the theoretical yields of liquid and solid products from the fast pyrolysis operation. Considering the fact that highly torrefied biomass is less reactive, it is expected that LP-TC may give the lowest bio-oil yield under the identical pyrolysis conditions.

Similar to other work (Bourgois and Guyonnet, 1988), this study showed that torrefaction produces solid fuel with decreased oxygen and increased carbon contents. As shown in Table 2, the oxygen-to-carbon ratio is 0.64 for LP-Raw, followed by 0.53 for LP-TA, 0.48 for LP-TB, and 0.33 for LP-TC. Therefore, the quality of pyrolysis feedstock has been improved by torrefaction pretreatment in terms of oxygen-to-carbon ratio. As a result, the high heating value increases with the reduced oxygen content in torrefied wood. In addition, the slightly reduced hydrogen content and increased nitrogen content were not significant after torrefaction pretreatment.

3.2. Fast pyrolysis operation and its mass balance

Bio-oil, bio-char and non-condensable gas (NCG) are the major products obtained from a fast pyrolysis process. In this study, the yield of bio-oil and bio-char was determined by weight and the gas yield was estimated by difference. All yield results shown in Table 3 were calculated based on the air-dry mass of biomass.

As shown in Table 3, as the torrefaction severity increases, the total bio-oil yield is reduced and the yield of bio-char is increased. Non-torrefied wood achieves the highest bio-oil yield; LP-TA and LP-TB attain similar capacity of bio-oil production. It is not surprising to see that the severely torrefied wood produces only 33.5% total bio-oil since some thermally-reactive components have been removed in the torrefaction process as confirmed by the lower amount of volatiles in the proximate analysis for LP-TC. To increase the bio-oil yield for LP-TC, different pyrolysis conditions such as a higher temperature with longer residence time might be necessary. The heating value of the bio-oil produced from torrefied wood is higher than that from raw wood materials. However, when comparing the heating value of bio-oil (dry base) to its pyrolysis feedstock, only LP-TC oil shows higher value than its starting material; while the heating value of the other two bio-oils are slightly lower than that of their torrefied raw materials. Clearly, BOC has a much higher weight and water content than BOP as listed in Table 3. Also, bio-oils from torrefied wood generally have less water content than that from raw wood. Compared to that of LP-TA and LP-TB, the lower bio-oil yield of LP-TC can be explained by the loss of BOC since the amount of BOC for LP-TC is less than half of that collected from LP-TA and LP-TB. It is assumed that the condenser mainly collects the low molecular weight molecules, such as water and acids from the stream of the volatile gas. The electric-precipitator, however, is much more effective at collecting higher molecular weight molecules such as sugar and pyrolytic lignin. Those low molecular weight molecules in BOC may be the primary degradation products from the hemicelluloses and cellulose; therefore the low amount of BOC for LP-TC is reasonable.

Table 3
Amount of pyrolysis bio-oil and bio-char produced from torrefied wood. The values are based on 100 g of air-dry biomass introduced.

Sample ID	Bio-oil (g)			HHV[c] (MJ/kg)	Water in bio-oil (%)		Biochar (g)	Gas (g)
	BOC[a]	BOP[b]	Total	MBO[d]	BOC[a]	BOP[b]		
LP-Raw	44.3	22.9	67.2	21.0 (15.4)	44.4	14.3	9.7	23.1
LP-TA	37.1	17.4	54.5	21.2 (16.6)	36.7	8.46	22.2	23.3
LP-TB	33.5	18.6	52.1	23.5 (18.0)	41.3	9.04	27.0	20.9
LP-TC	17.9	15.6	33.5	28.7 (24.3)	35.7	6.29	43.3	23.2

[a] BOC: bio-oil collected from first condenser.
[b] BOP: bio-oil collected from electrostatic precipitator.
[c] HHV: high heating value based on dry bio-oil (wet-based HHV in parentheses).
[d] MBO: high heating value was measured on mixed BOC and BOP.

Table 4
Conversion yield of carbon and oxygen from biomass to pyrolysis products.

		Biomass	BOC[a]	BOP[b]	Bio-oil	Biochar	NCG[c]
C (%)	LP-Raw	100	30.1	27.8	57.9	17.5	24.6
	LP-TA	100	23.4	20.5	43.9	40.0	16.1
	LP-TB	100	15.9	26.0	41.9	45.1	13.0
	LP-TC	100	6.6	18.5	25.1	51.1	23.8
O (%)	LP-Raw	100	54.9	19.3	74.2	6.6	19.2
	LP-TA	100	47.7	17.0	64.7	7.2	28.1
	LP-TB	100	40.2	24.3	64.5	7.0	28.5
	LP-TC	100	20.3	20.2	40.5	21.0	38.5

[a] BOC: bio-oil collected from first condenser.
[b] BOP: bio-oil collected from electrostatic precipitator.
[c] NCG: non-condensable gas.

Table 4 presents the results of the mass conversion for carbon and oxygen in fast pyrolysis of torrefied feedstocks based on elemental analysis. These results show how torrefaction affects the elemental distribution in pyrolysis products and discloses the reason as to why bio-oil, with a low oxygen-to-carbon ratio, can be produced via torrefaction. Of all of the carbon in LP-Raw, 57.9% went to bio-oil, 17.5% to bio-char and 24.6% to NCG. For torrefied wood, however, less carbon was converted into bio-oil components and most of it is retained in bio-char. The low carbon conversion to bio-oil for torrefied wood suggests that thermally treated wood is less reactive at the same pyrolysis conditions. The oxygen conversion in fast pyrolysis affects the oxygen content in bio-oil. As shown in Table 4, 74.2% of the oxygen went to bio-oil made from LP-Raw, while the pyrolysis of LP-TA and LP-TB gave 64.7 and 57.0% of oxygen resulted in the bio-oil respectively. In the case of fast pyrolysis of LP-TC, only 43.1% of oxygen in wood was transformed into bio-oil, but a noticeably higher amount of oxygen went into bio-char and NCG compared to that for the mild torrefied sample. Both carbon and oxygen conversion from pyrolysis feedstock to bio-oil shows a decreasing trend from raw biomass to severely torrefied wood, and the reduction rate is higher for carbon conversion than that for oxygen conversion.

3.3. Bio-oil characterization: Elemental and chemical analyses

Fig. 2 compares the oxygen-to-carbon ratio and the effective hydrogen-to-carbon ratio of bio-oils pyrolyzed from torrefied wood to those of non-torrefied wood. The definition of effective hydrogen-to-carbon ratio is expressed in Eq.1. Where, nH, nO and nC are the mole numbers of hydrogen, oxygen and carbon respectively. This term eliminates the hydrogen contribution of water to the overall hydrogen to carbon ratio and it is a useful indicator in the field of bio-oil hydrotreating. (Vispute et al., 2010)

$$H/C_{eff} = (n_H - 2n_o)/n_c \tag{1}$$

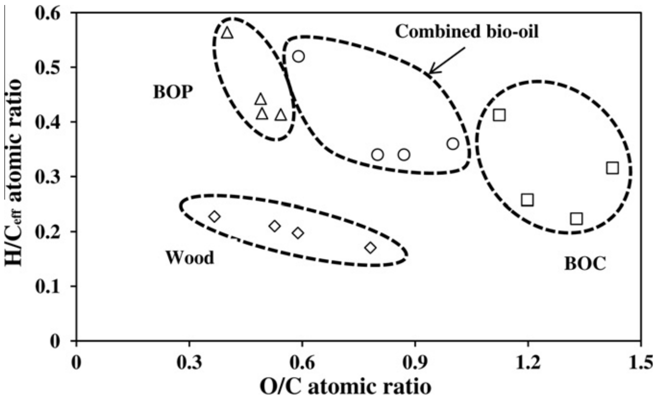

Fig. 2. Elemental analysis of bio-oils and wood: oxygen-to-carbon ratio vs. hydrogen-to-carbon effective ratio. Within these groups, the four points from right to left represent LP-Raw, LP-TA, LP-TB and LP-TC. Combined bio-oil indicates the mixed BOC and BOP.

As shown in Fig. 2, there is clear evidence that the oxygen-to-carbon ratio decreases with effective hydrogen-to-carbon ratio as the raw wood materials go through more intense torrefaction. Similarly, the bio-oils such as BOC, BOP, and their combined mixture (MBO) inherit these features from their feedstocks. Additionally, the BOP not only preserves the reduced oxygen to carbon ratio from their starting wood materials, but also their absolute ratio is lower than that of the raw wood material. This is especially true for the BOP produced from the LP-Raw, LP-TA and LP-TB samples. The reason for this reduction of oxygen-to-carbon ratio in BOP might be due to the configuration of the bio-oil collection system. When volatile gases pass the cold condenser, most of the low molecular oxygenates with high oxygen-to-carbon ratios will be retained in the BOC condenser; therefore fewer of them would flow into the ESP system. In addition, both BOC and BOP show improvement on the effective hydrogen-to-carbon effective ratio with an increasing torrefaction severity of the fast pyrolysis feedstock. This increase may suggest that lower hydrogen consumption during a hydrotreating process for bio-oil upgrading would be required.

Low molecular weight (<550 Da) compounds obtained from pyrolysis of wood are often easily identified by gas chromatography followed by mass spectroscopy (GC/MS) (Ralph and Hatfield, 1991). Although GC/MS has a limitation in that only a portion of components in the bio-oil can be detected because of sample volatility requirements, this analysis is still accepted as a powerful technology for bio-oil characterization.

Due to the apparent differences between the two fractions of bio-oil as discussed above, the BOC and BOP samples were analyzed separately. Figs. S1 and S2 (Supplementary Materials) show total ion chromatograms for BOC and BOP produced from LP-Raw and LP-TC, respectively. More than one hundred components of the bio-oil were identified by searching the NIST 2008 MS library and were confirmed with standard chemical retention time and other references (Pouwels et al., 1989; Faix et al., 1991; Reeves and Galletti, 1993; Marsman et al., 2007; Mullen and Boateng, 2008; Nowakowski et al., 2010).

To visualize the changes of the functional group composition in bio-oil as a function of torrefaction severity, a summary of the relevant chromatographic peaks is presented in Fig. 3. In this figure, the chemicals have been classified into ten groups including esters, alcohols, aldehydes, ketones, acids, furanics, pyranics, anhydrosugars, phenolics and other unidentified oxygenates. For additional details, Tables 5 and 6 list the major compounds and their area percentages obtained from the chromatograms for BOC and BOP, respectively. These chemicals are arranged in a decreasing order according to their peak area occupancy for each bio-oil species. It is worthwhile noting that about 95% of the total area of the chromatograms was identified. Generally, it was found that the difficulties in the identification were mainly due to overlapping peaks and low signal to noise ratios.

A distinct compositional variation can be noticed in BOC and BOP when comparing the bio-oils having the same feedstock origin. In BOC, esters, aldehydes, ketones, acids, furanics, pyranics, anhdyrosugars and phenolics are the major components with relatively few alcohols. All of these chemicals are evenly weighted (10–20%). Conversely, furanics, anhydrosugars, pyranics, and especially phenolics (up to 50% for BOP from LP-TC) are abundant in BOP. When comparing the composition of torrefaction based bio-oil to that of the raw material, both BOC and BOP pyrolyzed from torrefied wood are generally rich in pyrolytic lignin and anhydrosugars but lack light oxygenates such as acids and aldehydes and the most

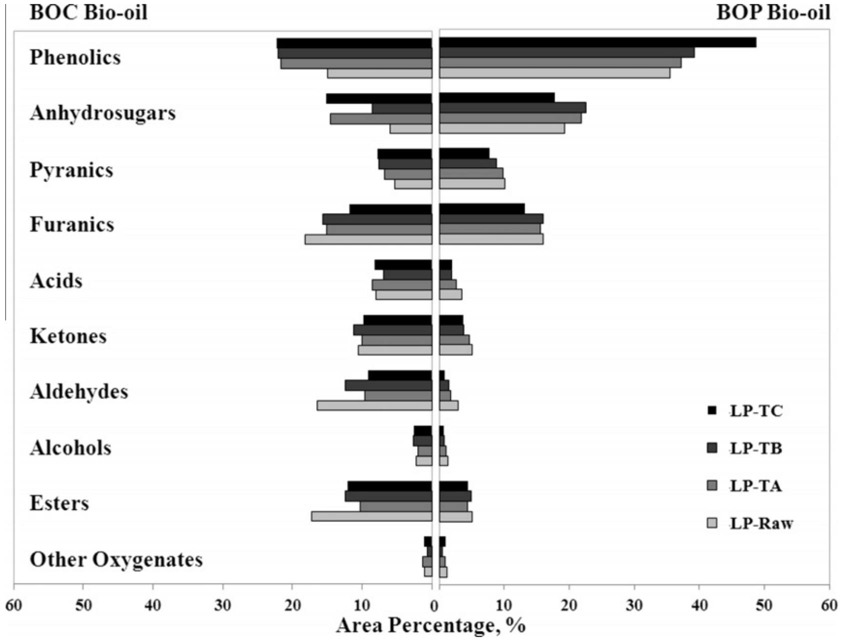

Fig. 3. Summary of chemical compositions of bio-oils produced from LP-Raw, LP-TA, LP-TB and LP-TC (bottom to top within each chemical group) for BOC (left) and BOP (right).

Table 5
Major chemical compounds in BOC as determined by GC/MS.

	BOC-LP-Raw		BOC-LP-TA		BOC-LP-TB		BOC-LP-TC	
	Chemicals	Area (%)	Chemicals	Area (%)	Chemicals	Area (%)	Chemicals	Area (%)
1	Glycolaldehyde	12.90	1,6-Anhydro-β-D-glucopyranose	9.84	Glycolaldehyde	8.56	1,6-Anhydro-β-D-glucopyranose	11.21
2	Acetyloxyacetaldehyde	12.80	Glycolaldehyde	6.78	Acetyloxyacetaldehyde	8.03	Acetyloxyacetaldehyde	7.89
3	Acetol	7.32	Acetol	5.70	Acetol	6.19	Glycolaldehyde	6.88
4	Acetic acid	6.56	Acetic acid	5.68	1,6-anhydro-β-D-glucopyranose	5.68	Acetic acid	5.49
5	3,4-Furandiol, tetrahydro	5.82	Acetyloxyacetaldehyde	5.26	Acetic acid	5.14	Acetol	5.46
6	1,6-anhydro-β-D-glucopyranose	4.51	3,4-Furandiol, tetrahydro	2.71	Phenol, 2-methoxy-4-methyl-	4.37	Phenol	3.18
7	Butanedial	2.90	Phenol, 2-methoxy-4-methyl-	2.57	3,4-Furandiol, tetrahydro	3.64	*p*-Cresol and m-Cresol (overlapped)	3.12
8	Pyruvic acid methyl ester	2.63	Butanedial	2.28	Butanedial	3.31	3,4-Furandiol, tetrahydro	3.00
9	2,5-Dihydro-5-methylfuran-2-one	2.41	Guaiacol	2.05	2,5-Dihydro-5-methylfuran-2-one	2.95	1,2-Benzenediol	2.93
10	Phenol, 2-methoxy-4-methyl-	1.99	2,5-Dihydro-5-methylfuran-2-one	1.93	Guaiacol	2.80	*p*-Ethylguaiacol	2.42
11	Furfural	1.92	Pyruvic acid methyl ester	1.91	Methyl-dihydro-(2H)-pyran-2-one	2.42	Methyl-dihydro-(2H)-pyran-2-one	2.37
12	Guaiacol	1.84	Furfural	1.89	Pyruvic acid methyl ester	2.34	Butanedial	2.04
13	5 -Hydroxymethyl-2 -furaldehy de	1.70	Methyl-dihydro-(2H)-pyran-2-one	1.86	2-Methoxy-4-vinylphenol	2.22	Unknown	1.63
14	Methyl-dihydro-(2H)-pyran-2-one	1.56	5-Hydroxymethyl-2-furaldehyde	1.83	1-Acetyloxypropan-2-one	1.99	Pyruvic acid methyl ester	1.56
15	2(5H)-Furanone	1.55	Phenol	1.58	2(5H)-Furanone	1.64	1-Acetyloxypropan-2-one	1.50
16	Phenol	1.14	2(5H)-Furanone	1.35	Furfural	1.52	Propanal, 2,3-dihydroxy-	1.42
17	*p*-Cresol and m-Cresol (overlapped)	1.11	1 -Acetyloxypropan-2-one	1.31	Phenol	1.52	*o*-Cresol	1.36
18			Unknown	1.31	*p*-Ethylguaiacol	1.51	Furfural	1.31
19			Isoeugenol	1.28	*o*-Cresol	1.34	1,2-Benzenediol, 4-methyl-	1.29
20			*o*-Cresol	1.21	Isoeugenol	1.22	2(5H)-Furanone	1.25
21			1,2-Benzenediol	1.15	5-Hydroxymethyl-2-furaldehyde	1.17	Phenol, 2,3-dimethyl	1.24
22			Formic acid	1.11	Unknown	1.12	Guaiacol	1.02
23					Propanal, 2,3-dihydroxy-	1.02	Unknown	1.01
Cumulative area (%)		70.60		62.59		71.7		70.58

consistent trend in Fig. 3 is the increasing amount of lignin oligomers and anhydrosugars from LP-Raw to LP-TC.

The varied composition of bio-oils from torrefied wood can be attributed to two aspects. On the one hand, torrefaction pretreat-

Table 6
Major chemical compounds in BOP as determined by GC/MS.

	BOP-LP-Raw		BOP-LP-TA		BOP-LP-TB		BOP-LP-TC	
	Chemicals	Area (%)	Chemicals	Area (%)	Chemicals	Area (%)	Chemicals	Area (%)
1	1,6-Anhydro-β-D-glucopyranose	13.91	1,6-Anhydro-β-D-glucopyranose	14.74	1,6-Anhydro-β-D-glucopyranose	13.44	1,6-Anhydro-β-D-glucopyranose	12.46
2	5-Hydroxymethyl-2-furaldehyde	3.28	Phenol, 2-methoxy-4-methyl-	4.19	Phenol, 2-methoxy-4-methyl-	6.15	1,2-Benzenediol	4.87
3	Phenol, 2-methoxy-4-methyl-	2.80	Methyl-dihydro-(2H)-pyran-2-one	2.88	2-Methoxy-4-vinylphenol	3.76	*m*-Cresol and *p*-cresol (overlapped)	4.43
4	Isoeugenol	2.78	Isoeugenol	2.81	Isoeugenol	3.64	1,2-Benzenediol, 3-methyl	3.80
5	2,5-Dihydro-5-methylfuran-2-one	2.38	Guaiacol	2.67	Guaiacol	3.27	Phenol	3.10
6	Acetol	2.36	2-Methoxy-4-vinylphenol	2.59	Methyl-dihydro-(2H)-pyran-2-one	2.40	Methyl-dihydro-(2H)-pyran-2-one	2.69
7	Acetic acid	2.19	5-Hydroxymethyl-2-furaldehyde	2.45	5-Hydroxymethyl-2-tetrahydro-furaldehyde-3-one	2.39	5-Hydroxymethyl-2-tetrahydro-furaldehyde-3-one	2.64
8	Guaiacol	2.18	*m*-Cresol and *p*-Cresol (overlapped)	2.41	2,5-Dihydro-5-methylfuran-2-one	2.32	Phenol, 2,3-dimethyl	2.30
9	Acetyloxyacetaldehyde	2.16	2,5-Dihydro-5-methylfuran-2-one	2.33	5-Hydroxymethyl-2-furaldehyde	2.29	Phenol, 2-methoxy-4-methyl-	2.27
10	Glycolaldehyde	2.08	5-Hydroxymethyl-2-tetrahydro-furaldehyde-3-one	1.97	*m*-Cresol and *p*-Cresol (overlapped)	1.94	*o*-Cresol	1.83
11	Vanilla	2.06	Acetic acid	1.89	Unknown	1.61	*p*-Ethylguaiacol	1.77
12	Methyl-dihydro-(2H)-pyran-2-one	2.05	1,2-Benzenediol	1.87	Acetol	1.46	Guaiacol	1.65
13	*p*-Ethylguaiacol	1.94	Unknown	1.81	Furfural	1.44	5-Hydroxymethyl-2-furaldehyde	1.56
14	Tetrahydropyran-2-carbinol	1.70	Acetol	1.75	1,6-Anhydro-β-D-galactofuranose	1.42	Unknown	1.50
15	Furfural	1.69	Phenol	1.74	Phenol	1.41	Unknown	1.46
16	Unknown	1.48	Phenol, 2,3-dimethyl	1.69	Acetic acid	1.39	Furfural	1.37
17	Eugenol	1.44	Furfural	1.64	Acetyloxyacetaldehyde	1.38	Acetic acid	1.35
18	*m*-Cresol and *p*-Cresol (overlapped)	1.42	1,6-Anhydro-β-D-galactofuranose	1.43	*p*-Ethylguaiacol	1.35	2,5-Dihydro-5-methylfuran-2-one	1.29
19	1,2-Benzenediol	1.37	Eugenol	1.33	Unknown	1.31	Acetol	1.09
20	2H-Pyran, 3,4-dihydro-2-methoxy-	1.35	Vanilla	1.26	1,2-Benzenediol	1.30	Acetyloxyacetaldehyde	1.08
21	1,6-anhydro-β-D-galactofuranose	1.34	2(5H)-Furanone	1.20	Phenol, 2,3-dimethyl	1.29	2,3,5-Trimethyl phenol	1.01
22	2(5H)-Furanone	1.29	Glycolaldehyde	1.16	Unknown	1.20		
23	Phenol, 2,3-dimethyl	1.19	*o*-Cresol	1.15	2(5H)-Furanone	1.19		
24	1 -Acetyloxypropan-2-one	1.13	Acetyloxyacetaldehyde	1.14	Eugenol	1.19		
25	Phenol	1.11	Unknown	1.13	Vanilla	1.14		
26	5-Hydroxymethyl-2-tetrahydro-furaldehyde-3-one	1.04	(4)-Methyltetrahydrofuran-3-one	1.10	1-Acetyloxypropan-2-one	1.05		
27	Acetoguaiacone	1.03	*p*-Ethylguaiacol	1.09				
Cumulative area (%)		60.75		63.42		62.73		55.52

ment alters the composition of torrefied wood, resulting in less holocellulose but more lignin residues. Therefore, after fast pyrolysis, a reduced amount of light oxygenates from cellulose and hemicellulose will be presented in bio-oil while pyrolytic lignin becomes more concentrated. On the other hand, the mild thermal pretreatment may modify the structure and chemistry of the wood components and change their reaction pathways in fast pyrolysis. These modifications may favor the formation of certain bio-oil compounds. In addition, this may lead to the formation of certain chemical species that do not exist in bio-oil from non-treated biomass. By comparing GC/MS data shown in Figs. S1 and S2 (Supplementary Materials), together with detailed GC/MS identification (partially shown in Tables 5 and 6), it is found that all of the major bio-oil compounds that have been identified in LP-Raw also exist in bio-oils pyrolyzed from torrefied wood. The only difference is the quantity of these species. Indeed, there are some minor components having unique peaks in the chromatograms of bio-oils pyrolyzed from torrefied wood which have not been identified. These peaks may be new bio-oil species resulting from the torrefaction pretreatment, but, the compounds are relatively insignificant due to their extremely low area occupancy in the chromatograms. Therefore, it may be concluded that torrefaction mainly change the bio-oil composition in terms of the quantities of same oil species rather than producing significant amount of novel bio-oil compounds. However, it is worth noting that the detected species by GC/MS are only a portion of the bio-oil composition (GC-visible) and the newly created bio-oil compounds may exist in the GC-invisible portion. Therefore, the possibility of significant species difference within the composition of these bio-oils cannot be ruled out.

4. Conclusions

Pyrolysis bio-oils produced from torrefied loblolly pine feature reduced oxygen-to-carbon ratios and water content, which are beneficial for downstream processes such as hydrotreating and hydrocracking. However, these reductions are realized with the penalty of bio-oil yield due to the increased thermal resistance of torrefied biomass at the same pyrolysis conditions. Based on the

GC/MS analysis, the chemical composition of bio-oils produced from torrefied biomass shows a high quantity of pyrolytic lignin compounds, which indicated that they have good potential for phenolic-based chemical production. In summary, torrefaction is considered as an effective pretreatment strategy for fast pyrolysis to produce high quality bio-oil.

Acknowledgements

Authors would like to thank Chris Hopkins at North Carolina State University for torrefaction operation to produce torrefied wood and Steve Kelley for his valuable comments during the work. This work is supported by the National Science Foundation under Grant No. 0832498.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2012.01.159.

References

Acharjee, T.C., Coronella, C.J., Vasquez, V.R., 2011. Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass. Bioresour. Technol. 102, 4849–4854.

Almeida, G., Brito, J.O., Perré, P., 2010. Alterations in energy properties of eucalyptus wood and bark subjected to torrefaction: the potential of mass loss as a synthetic indicator. Bioresour. Technol. 101, 9778–9784.

Bourgois, J., Guyonnet, R., 1988. Characterization and analysis of torrefied wood. Wood Sci. Technol. 22, 143–155.

Couhert, C., Salvador, S., Commandré, J.-M., 2009. Impact of torrefaction on syngas production from wood. Fuel 88, 2286–2290.

Czernik, S., Bridgwater, A.V., 2004. Overview of applications of biomass fast pyrolysis oil. Energy Fuels 18, 590–598.

Dence, C.W., 1992. The determination of lignin. In: Lin, S.Y., Dence, C.W. (Eds.), Method in Lignin Chemistry. Springer-Verlag, Berlin Heidelberg, pp. 33–61.

Demirbas, A., 2004. Effect of initial moisture content on the yields of oily products from pyrolysis of biomass. J. Anal. Appl. Pyrolysis. 71, 803–815.

Diebold, P.J., 2002. A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils. In: Bridgwater, A.V. (Ed.), Fast Pyrolysis of Biomass: A handbook. CPL Press, Newbury, U.K., pp. 205–241.

Elliott, D.C., Hart, T.R., 2009. Catalytic hydroprocessing of chemical models for bio-oil. Energy Fuels 23, 631–637.

Elliott, D.C., 2007. Historical developments in hydroprocessing bio-oils. Energy Fuels 21, 1792–1815.

Faix, O., Fortmann, I., Bremer, J., Meier, D., 1991. Thermal degradation products of wood - gas chromatographic separation and mass spectrometric characterization of polysaccharide derived products. Eur. J. Wood Wood Prod. 49, 213–219.

Marsman, J., Wildschut, J., Mahfud, F., Heeres, H., 2007. Identification of components in fast pyrolysis oil and upgraded products by comprehensive two-dimensional gas chromatography and flame ionisation detection. J. Chromatogr. A. 1150, 21–27.

Mohan, D., Pittman Jr., C.U., Steele, P.H., 2006. Pyrolysis of wood/biomass for bio-oil: a critical review. Energy Fuels 20, 848–889.

Mullen, C.A., Boateng, A.A., 2008. Chemical composition of bio-oils produced by fast pyrolysis of two energy crops. Energy Fuels 22, 2104–2109.

Nowakowski, D.J., Bridgwater, A.V., Elliott, D.C., Meier, D., de Wild, P., 2010. Lignin fast pyrolysis: results from an international collaboration. J. Anal. Appl. Pyrolysis. 88, 53–72.

Phanphanich, M., Mani, S., 2011. Impact of torrefaction on the grindability and fuel characteristics of forest biomass. Bioresour. Technol. 102, 1246–1253.

Pouwels, A.D., Eijkel, G.B., Boon, J.J., 1989. Curie-point pyrolysis-capillary gas chromatography–high-resolution mass spectrometry of microcrystalline cellulose. J. Anal. Appl. Pyrolysis. 14, 237–280.

Prins, M.J., Ptasinski, K.J., Janssen, F.J.J.G., 2006a. More efficient biomass gasification via torrefaction. Energy 31, 3458–3470.

Prins, M.J., Ptasinski, K.J., Janssen, F.J.J.G., 2006b. Torrefaction of wood part 2 analysis of products. J. Anal. Appl. Pyrolysis. 77, 35–40.

Ralph, J., Hatfield, R.D., 1991. Pyrolysis-gc-ms characterization of forage materials. J. Agric. Food Chem. 39, 1426–1437.

Reijnders, L., 2006. Conditions for the sustainability of biomass based fuel use. Energy Policy 34, 863–876.

Reeves III, J.B., Galletti, G.C., 1993. Use of pyrolysis—gas chromatography/mass spectrometry in the study of lignin assays. J. Anal. Appl. Pyrolysis. 24, 243–255.

Repellin, V., Govi, A., Rolland, M., Guyonnet, R., 2010. Energy requirement for fine grinding of torrefied wood. Biomass Bioenergy. 34, 923–930.

Sharma, R.K., Bakhshi, N.N., 1993. Catalytic upgrading of pyrolysis oil. Energy Fuels 7, 306–314.

Sluiter A., Hames, B., Ruiz, R., Scarlata, C., Sluiter. J., Templeton, D., Crocker, D., 2008. NREL Laboratory Analytical Procedure. NREL/TP-510-42618, pp. 1-18.Retrieved from <http://www.nrel.gov/biomass/pdfs/42618.pdf>.

Vispute, T.P., Zhang, H., Sanna, A., Xiao, R., Huber, G.W., 2010. Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. Science 330, 1222–1227.

Yan, W., Hastings, J.T., Acharjee, T.C., Coronella, C.J., Vásquez, V.R., 2010. Mass and energy balances of wet torrefaction of lignocellulosic biomass. Energy Fuels 24, 4738–4742.

Yan, W., Acharjee, T.C., Coronella, C.J., Vásquez, V.R., 2009. Thermal pretreatment of lignocellulosic biomass. Environ. Prog. Sustainable Energy 28, 435–440.

Zwart, R.W., Boerrigter, H., Van der Drift, A., 2006. The impact of biomass pretreatment on the feasibility of overseas biomass conversion to fischer—tropsch products. Energy Fuels 20, 2192–2197.